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Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future**

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An overview of one of the most successful conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDT) and its derivatives, is presented, detailing its early development, the synthesis of numerous hybrid and derivative materials, along with a description of the broad array of properties accessible and a description of a set of the more prominent applications in which they can be utilized. Synthetic flexibility and facility is the key to the many new 3,4-ethylenedioxythiophene- (EDT-) based monomers, oligomers, and (co)polymers. These (co)polymers provide highly conducting and especially stable doped states, a range of optical properties with electronic bandgaps varying across the entire visible spectrum, and enhanced redox properties, making them useful for numerous electrochemical devices. Present and future applications for PEDT that are discussed include static charge dissipation films and electrode materials in solid electrolyte capacitors.

*Dedicated to Prof. H.-J. Rosenkranz on the occasion of his 60th birthday*

1. Introduction

Since Shirakawa et al.[1] discovered that polyacetylene can reach extremely high electrical conductivities, the field of conducting polymers, which are often referred to as synthetic metals, has attracted the interest of thousands of scientists.[2] Much of the combined research efforts of industrial, academic, and government researchers have been directed toward developing materials that are application stable in the conducting state, easily processable, and relatively simple to produce at low cost. With the many difficulties encountered in accomplishing these goals, only recently, companies have been able to bring products to the market.

Of the many interesting conducting polymers that have been developed over the past 25 years, those based on polyanilines, polypyrroles, polythiophenes, polyphenylenes, and poly(p-phenylene vinylene)s have attracted the most attention.[2,3] Of these, the polyaniline family stands out for its ability to form processable conductive forms at relatively low cost and in bulk amounts.[4] Unfortunately, due to the possible presence of benzidine moieties in the polymer backbone, which might yield toxic (carcinogenic) products upon degradation,[5] numerous industrial and academic

groups have limited their research in polyaniline chemistry. While the (hetero)aromatic polypyrrole and polythiophene, as well as poly(p-phenylene vinylene), are possibly more environmentally "friendly" systems, they have the disadvantage of being insoluble and infusible. In order to overcome these problems, numerous substituted derivatives of these polymers have been developed that carry alkyl, alkoxy, and other substituents along their backbones.[3,6] By controlling main-chain architecture (e.g., regioregularity[6,7]) and pendant group chemistry (e.g., water-soluble sulfonates[6a,8]), a broad variety of properties were made available from the parent systems. Although these side-chains provide a level of control of both the physical and electronic properties, often the ultimate accessible electronic properties were degraded relative to the parent.

During the second half of the 1980s, scientists at the Bayer AG research laboratories in Germany developed a new polythiophene derivative, poly(3,4-ethylenedioxythiophene), having the backbone structure shown below.[9]
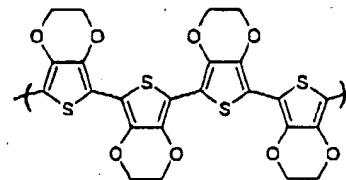
PEDT

This polymer, often abbreviated as PEDT or PEDOT, was initially developed to give a soluble conducting polymer that lacked the presence of undesired α,β- and β,β-couplings within the polymer backbone. Prepared using standard oxidative chemical or electrochemical polymerization

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methods, PEDT was initially found to be an insoluble polymer, yet exhibited some very interesting properties. In addition to a very high conductivity (ca. 300 S/cm), PEDT was found to be almost transparent in thin, oxidized films and showed a very high stability in the oxidized state.[9,10] The solubility problem was subsequently circumvented by using a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS), as the charge-balancing dopant during polymerization to yield PEDT/PSS. This combination resulted in a water-soluble polyelectrolyte system with good film-

forming properties, high conductivity (ca. 10 S/cm), high visible light transmissivity, and excellent stability.[11] Films of PEDT/PSS can be heated in air at 100 °C for over 1000 h with only a minimal change in conductivity. With this new system, now known under its commercial name BAYTRON P (P stands for polymer), Bayer researchers have been able to develop several applications. Although initially used as an antistatic coating in photographic films from AGFA, several new applications have been implemented over the past few years (e.g., electrode material in capaci-

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Friedrich Jonas completed his Ph.D. in 1980 at the Rheinisch Westfälische Technische Hochschule Aachen with a thesis on the synthesis of heterocycles. After that he joined Bayer's Central R&D Laboratories in Leverkusen where he began working on conducting organic materials. One of the results of this work is the development of 3,4-ethylenedioxythiophene.

Dieter Freitag studied chemistry in Freiburg and Frankfurt. After obtaining his Ph.D. in 1967, he joined Bayer's Central R&D Laboratories in 1968 working on polymer chemistry. In 1978 he became a group leader in the Plastics Business Group where he was responsible for research into new thermoplastics. In 1986 he moved to the Plastics Applications Department and in 1988 he was appointed Head of R&D of Bayer's Plastics Business group. In 1992 Dr. Freitag returned to Bayer's Central R&D Laboratories and has been leading the Materials Research Department there since 1994. Dr. Freitag was awarded the Otto Bayer Medal for his contributions to the research and development of thermoplastic polymers and the Hermann-F.-Mark Medal for his achievements in the field of engineering thermoplastics and especially polycarbonates.

Harald Pielartzik studied chemistry at the University of Dortmund and received his Ph.D. from the University of Saarland. In 1984 he joined Bayer's Central R&D Laboratories, working on thermoplastic materials with a special focus on functional polymers. In 1991 he transferred to Bayer's US subsidiary company Mobay (now Bayer Corp.) where he was responsible for the Polymer Reseach Group. Upon his return to Bayer's Central R&D Laboratories, he became Head of the Functional Materials Research Department.

John R. Reynolds is a Professor of Chemistry at the University of Florida with expertise in polymer chemistry and serves as an Associate Director for the Center for Macromolecular Science and Engineering. His research interests have involved electrically conducting and electroactive conjugated polymers for over 20 years with work focussed on the development of new polymers by manipulating their fundamental organic structure in order to control their ultimate properties. Reynolds obtained his M.S. (1982) and Ph.D. (1984) degrees from the University of Massachusetts in Polymer Science and Engineering. He has published over 100 peer-reviewed scientific papers and recently served as co-editor of the "Handbook of Conducting Polymers", which was published in 1998.
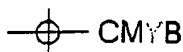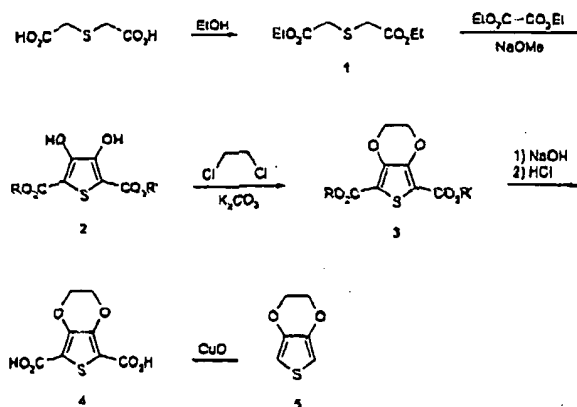
tors, material for through-hole plating of printed circuit boards), and more are expected.[11,12]

Driven by the properties and utility of PEDT/PSS, a number of research groups have entered the area of PEDT chemistry over the past decade. The latter has resulted in an exponential increase in the number of patents (ca. 70) and journal publications (ca. 180; see Fig. 1). This expanding interest is indicative of new materials, processes, devices, and in-place industrial applications. In this review, we focus on three aspects of PEDT chemistry. First, an overview will be given of the synthesis and characterization of EDT, PEDT, and numerous derivatives that have been reported. Subsequently, the properties (electrical, optical, electrochemical, etc.) of these systems will be discussed, bringing out some of the unique aspects that make this polymer especially useful. Finally, the presently industrially implemented and other applications under investigation of PEDT derivatives will be detailed. Since the field of PEDT chemistry is relatively young, this review will be accompanied by a relatively comprehensive list of patents and publications that have appeared over the past decade. We apologize in advance for any omissions we have made.
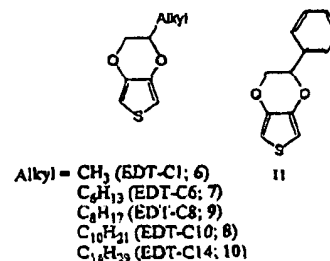
2. EDT and PEDT Synthesis and Characterization

2.1. 3,4-Ethylenedioxythiophene and Related, Substituted Derivatives

Although several routes towards EDT (5) are possible, Jonas et al. developed a synthetic strategy, shown in Scheme 1, starting from thiodiglycolic acid, based on the synthesis of 3,4-ethylenedioxythiophene-2,5-dicarboxylic acid (4) reported by Gogte et al.[13] Subsequent decarboxylation using a copper salt led to EDT in five steps.[9,14] EDT has a boiling point of 225 °C (1013 mbar) and slowly turns dark upon exposure to air and light due to partial oxidation. Bayer AG now produces EDT on a multi-ton scale,

Scheme 1. Synthesis of EDT (R, R' = Me or Et).

Alkyl = CH₃ (EDT-C1; 6)
C₆H₁₃ (EDT-C6; 7)
C₈H₁₇ (EDT-C8; 9)
C₁₀H₂₁ (EDT-C10; 8)
C₁₄H₂₉ (EDT-C14; 10)

and offers it commercially under its trade name BAYTRON M (M stands for monomer).

Capitalizing on the EDT core, a number of derivatives have been synthesized by various research groups. In 1992 Heywang and Jonas reported the synthesis of alkyl-substituted EDT derivatives EDT-C1 (6), EDT-C6 (7), and EDT-C10 (8).[9c] It should be noted that, using the same five-step strategy as described for EDT in Scheme 1, using 1,2-dibromoalkanes, as opposed to 1,2-dichloroethane, leads to relatively low overall yields in the Williamson ether step due to the use of a secondary bromide. In addition, the yields of the hydrolysis and decarboxylation steps
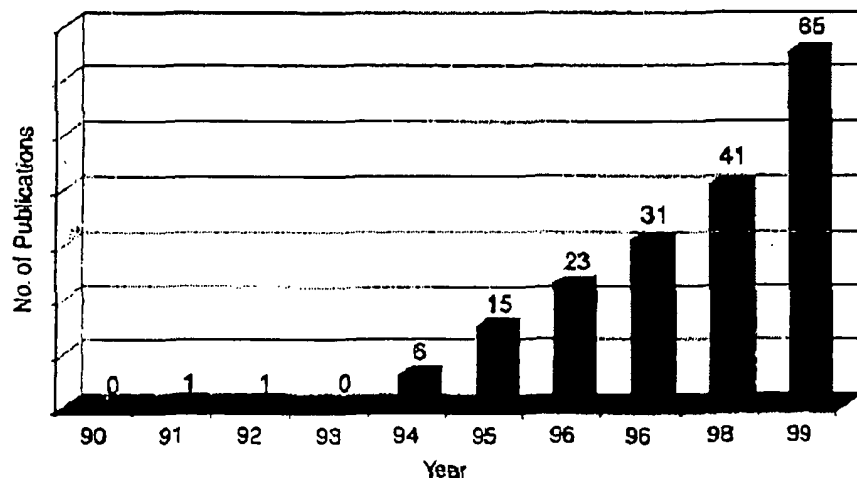
drastically decrease with increasing alkyl chain length as a result of the increasing lipophilicity of the molecules. Following this, Reynolds and co-workers reported on similar alkylated EDT derivatives (EDT-C8 (9) and EDT-C14 (10))[15,16] as well as the phenyl-substituted derivative EDT-C$_6$H$_5$ (11).[17]

Extending the pioneering work of Blohm et al.,[18] Ng et al. attempted the synthesis of the hydroxymethylated EDT derivative 12.[19] As shown in Scheme 2, reaction of epichlorohydrin with the dihydroxythiophene derivative 2 yielded a mixture of two isomers, including 12 and the hydroxylated 3,4-propylenedioxythiophene (ProDT) system 13.
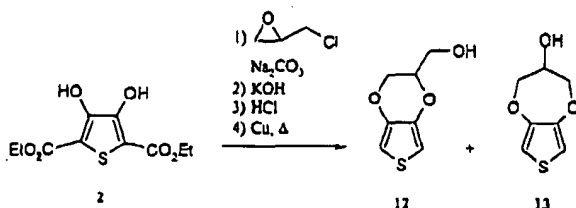

Scheme 2. Synthesis of hydroxymethylated 3,4-ethylenedioxythiophene (12).

Following this approach, Chevrot and co-workers applied a similar route and were able to separate the desired six-membered ring from its seven-membered isomer by chromatography.[20] This 3,4-ethylenedioxythiophene methanol (EDTM; 12) was subsequently converted to the water-soluble sodium salt of the butanesulfonic acid–functionalized EDT (EDTS; 14)[21] and into alkoxy-substituted EDT derivatives (15,16), as shown in Scheme 3.[22] Capitalizing on this chemistry and the original report of unsubstituted ProDT (17),[9,10] Reynolds and co-workers reported on several 3,4-alkylenedioxythiophenes, including BuDT (18), ProDT-Me (19), and the interesting phenyl derivative 20.[17]

To expand the range of substituted 3,4-alkylenedioxythiophenes available for the preparation of conducting and
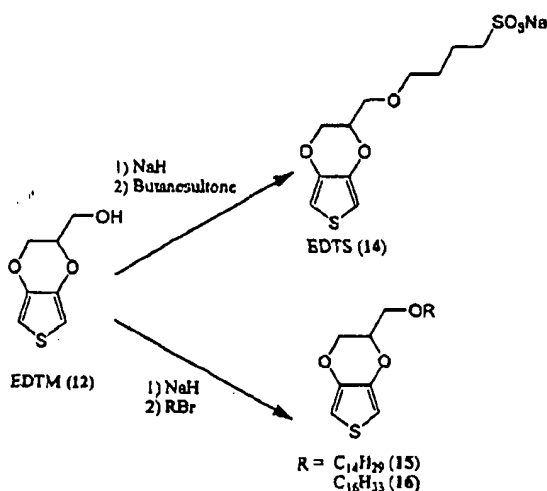
Scheme 3. Synthesis of sulfonatoalkoxy- and alkoxy-substituted EDT derivatives [20–22].
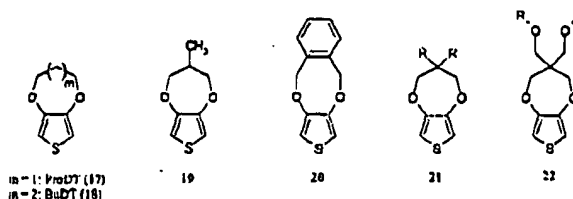
electroactive polymers, transetherification chemistry has been employed in monomer synthesis.[23,24] This has proven especially useful for preparing derivatives where steric interactions limit the utility of the double Williamson ether method for ring closure. In this manner, dialkyl derivatives of ProDT, including –CH$_3$, –C$_2$H$_5$, and –C$_8$H$_{17}$, and more complex ether pendants (22), have been prepared.[25] These polymers will provide special interest as the monomers are symmetrically derivatized and can provide regiosymmetrically substituted polymers that are sufficiently soluble to allow spin-coating to continuous films.

In developing a structural relative of EDT, Kanatzidis and co-workers reported the synthesis of 3,4-ethylenedithiathiophene (EDTT; 23) starting from 3,4-dibromothiophene as outlined in Scheme 4.[26] Although the yields accessible using this method were low, this provided the only example of an ethylenedithio-bridged thiophene that could be converted to an electroactive polymer. The later report of a high yield synthesis of 3,4-bis(isopropylthio)thiophene may provide another route to this family of polymers.[27]
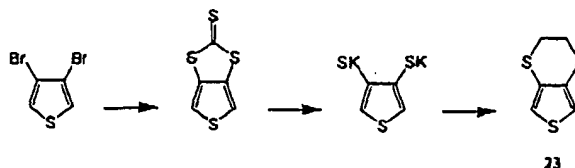
Scheme 4. Synthesis of 3,4-ethylenedithiathiophene (EDTT; 23) [26].

A last structural relative of EDT worth mentioning is 3,4-ethylenedioxypyrrole (EDP). This compound was first synthesized by Merz et al.[28] Due to its extreme electron richness, it easily oxidizes in air. Thus it has to be stored under argon at low temperatures; if not, it spontaneously polymerizes within a short time. Recently, Reynolds and co-workers reported the larger ring analogues of EDP.[29]

Characterization of EDT and its derivatives is relatively straightforward using all of the standard methods of molecular characterization. One fascinating aspect of EDT derivatives relates to their physical state, i.e., are they liquid or solid? As mentioned before, EDT is a colorless liquid; however, most of its derivatives are solids (e.g., EDTM,[30] EDTS, and ProDT). This simplifies their purification—crystallization as opposed to distillation or column chromatography. Furthermore, it enables the structural characterization of single crystals by X-ray crystallography.[17,31]

2.2. Oligo(3,4-ethylenedioxythiophene)s and Related Co-Oligomers

Oligo(3,4-ethylenedioxythiophene)s are quite difficult to prepare due to their low oxidation potentials. To date, only the dimer, 2,2'-bis(3,4-ethylenedioxythiophene) (bis-EDT; 24)[32,33] and the trimer 2,2':5',2''-ter(3,4-ethylenedioxythiophene) (ter-EDT; 25)[34] have been isolated. In a one-pot synthesis, dimer 24 was prepared by selective α-lithiation of EDT using "BuLi, followed by oxidative coupling using CuCl₂ (Scheme 5a); trimer 25 was obtained via a Kumada cross-coupling reaction (Scheme 5b). Due to their low oxidation potentials both oligomers oxidatively polymerize quite efficiently. The trimer even requires storage under an inert atmosphere at low temperature in order to prevent spontaneous polymerization.

In addition to bis-EDT 24 and ter-EDT 25,[35] the Reynolds research group has focussed studies on a series of bis-EDT–arylene multi-ring monomers (26) to provide polymers having a broad range of redox, optical, and electrochromic properties. A representative set of these are shown in Scheme 6 as synthesized via Kumada or Negishi cross-coupling reactions.[34,36]

These same concepts have been applied by others for the preparation of co-oligomers based on EDT. Zhu and Swager reported on the synthesis of 5,5'-bis(3,4-(ethylenedioxy) thien-2-yl)-2,2'-bipyridine **27** and 5,5'-bis(3,4:3',4'-bis(ethylenedioxy)[2,2'-bithiophen]-5-yl)-2,2'-bipyridine **28** using the Stille coupling methodology.[35] These two compounds have the ability to complex metal ions at the bipyridine unit, putting the metal ions in direct electronic communication with the conjugated backbone.[37] Metal-containing monomers have been reported using *N,N'*-ethylene-bis-(salicylidenimine)- or salen-based bis-EDT oligomers[38] (29), the tetrafulvalene-substituted dimer 30,[39] as well as the donor–acceptor system 31.[40] The latter system has proven especially interesting for the preparation of low bandgap polymers. Using this same concept, cyanovinylene-linked EDT oligomers 32 and 33 were prepared via a Knoevenagel condensation as donor–acceptor systems.[41] Combining the electronic benefits of EDT with the potential processability of an alkyl thiophene, Buvat and Hourquebie synthesized a dimer and trimer based on a combination of EDT and 3-octylthiophene.[42] Finally, Zotti et al. reported on the bis-EDT-acetylene oligomer,[43] whereas Cava and co-workers prepared several EDT-based oligomers using Wittig and Stille reactions.[44]
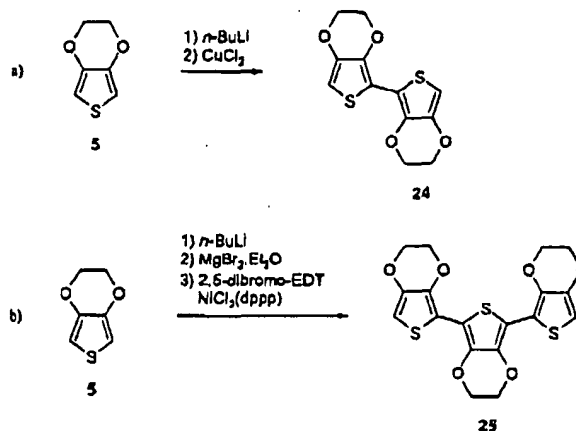
Scheme 5. Synthesis of: a) 2,2'-bis(3,4-ethylenedioxythiophene) (24) [32,33]; b) 2,2':5',2''-ter(3,4-ethylenedioxythiophene) (25) [34].
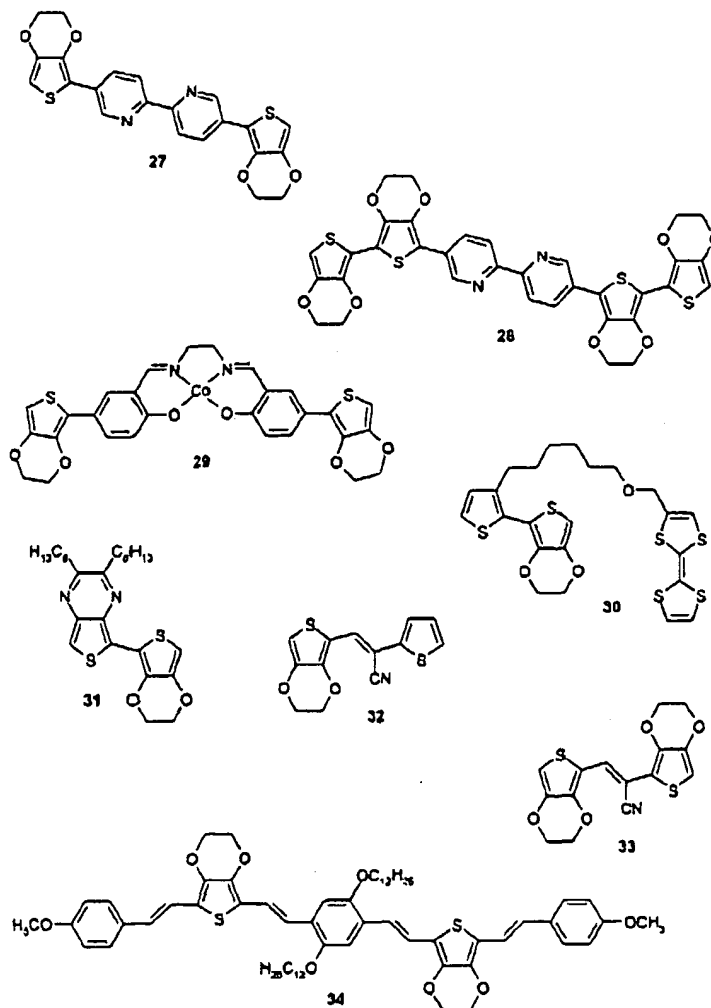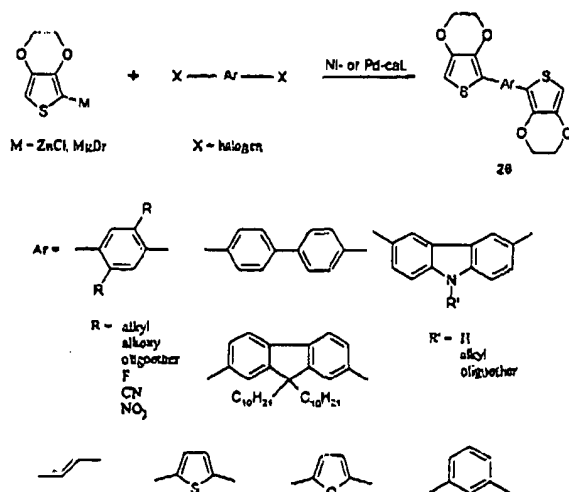
Scheme 6. Anthology of bis-EDT-arylene co-oligomers (26) as prepared by Kumuda and Negishi coupling reactions [34,36].

As with some of the single ring monomers 5–23, the multi-ring monomers 24–33 have been structurally analyzed. Furthermore, several oligomers have been characterized by X-ray crystallography.[36] These results demonstrate the subtle interplay between steric and electronic properties as the conjugated systems tend towards planarity with torsional interactions induced between rings by substituents of sufficient size. To the best of our knowledge, the EDT-containing oligomer 34 shown in Figure 2 represents the longest species reported to date. Interestingly, single crystals of 34 are quite planar with a deviation of only 4° observed using X-ray crystallography.[45]
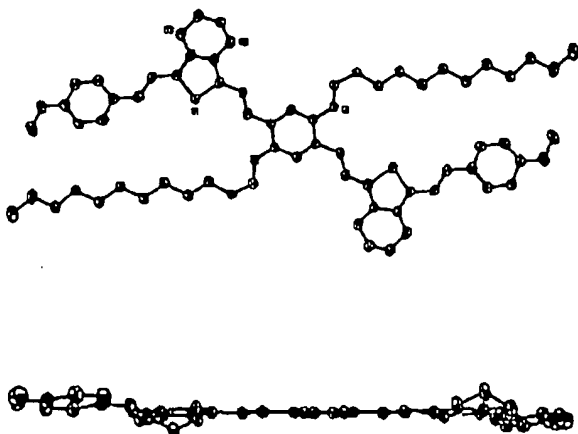

Fig. 2. X-ray crystal structure of oligomer 34 [45].

UV-vis spectroscopy of oligomeric EDT derivatives becomes more interesting with increasing conjugation length. Unfortunately, only very few data have been published to date using this characterization method. Table 1 shows a list of different oligomers, mostly bis-EDT derivatives, and their absorption maximum.

Table 1. UV-vis data of neutral oligo-EDT compounds (Ph = phenyl; Th = thienyl; F = furanyl; Carb = carbazoyl; ThPy = thienopyrazinyl). Solvent is $CHCl_3$ unless otherwise indicated.

Oligomer	Absorption maximum [nm]
EDT-EDT (24) [32]	320
EDT-EDT-EDT (25) [34,36]	400
EDT-Ph-EDT (26) [34,36]	344
EDT-Ph-Ph-EDT (26) [34,36]	342
EDT-Th-EDT (26) [34,36]	374
EDT-F-EDT (26) [34,36]	362
EDT-CH=CH-EDT (26) [34,36]	359
EDT-ThPy (31) [40]	456 [a]

[a] Solvent not mentioned.

Examination of the oxidation potentials (E_p in volts vs. Ag/Ag$^+$; note that all further electrochemical potentials are referenced to this) of EDT (5), bis-EDT (24), and ter-EDT (25), shows a linear relationship between E_p and the reciprocal number of EDT units: 1.1 V, 0.5 V, and 0.15 V, respectively. Extrapolation to an infinite number of EDT units gives an oxidation potential of –0.2 V for an infinite chain; the latter correlates well with the experimentally measured value determined for PEDT.[32] EDT and its derivatives electropolymerize efficiently to form electrode-supported films; under the proper conditions, free-standing films can be obtained.

2.3. Poly(3,4-ethylenedioxythiophene)s

The synthesis of PEDT derivatives can be divided into three different types of polymerization reactions:

- Oxidative chemical polymerization of the EDT-based monomers.
- Electrochemical polymerization of the EDT-based monomers.
- Transition metal–mediated coupling of dihalo derivatives of EDT.

2.3.1. Oxidative Chemical Polymerization of EDT-Based Monomers

Chemical polymerization of EDT derivatives can be carried out using several methods and oxidants. The classical method employs oxidizing agents such as $FeCl_3$ or $Fe(OTs)_3$.[46] Considering EDT itself, this method results in a black, insoluble and infusible compound, PEDT, that is difficult to characterize. However, as will be discussed in Section 3 below, this method can yield substrate-supported films with potentially useful electrical and optical properties.[9–12,47,48]

Chemical polymerization of alkylated[15–17,49] or alkoxy-lated[22] EDT derivatives (R ≥ $C_{10}H_{21}$) results in regio-random PEDT derivatives that are soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, and tetrahydrofuran (THF). As a result these polymers can be characterized

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using standard structural methods; for example, gel permeation chromatography (GPC) determined M_w values for a PEDT–$C_{14}H_{29}$ range from 10000–25000 g/mol (vs. polystyrene standards). Kumar and Reynolds demonstrated that by increasing the [FeCl$_3$]/[monomer] ratio to greater than two in the polymerization of EDT–$C_{14}H_{29}$, a fraction of the polymer becomes insoluble in organic solvents, which may be due to crosslinking.[16] At [FeCl$_3$]/[monomer] ratios greater than or equal to five, a fully insoluble polymer is formed.

A second polymerization method of EDT has been reported by de Leeuw et al.[50] Utilizing Fe^{III}(OTs)$_3$ at elevated temperature in combination with imidazole as a base (Scheme 7), resulted in a black insoluble and infusible PEDT film that, after rinsing with water and n-butanol, exhibited conductivities of up to 550 S/cm.[51]
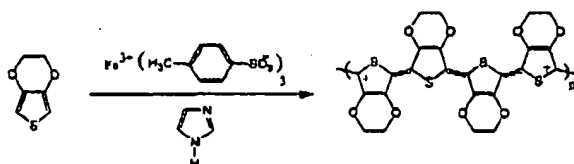
Scheme 7. Chemical polymerization of EDT as developed by de Leeuw et al. [50].

The third, and most practically useful, polymerization method for EDT is the so-called BAYTRON P synthesis that was developed at Bayer AG.[11,12] This method utilizes the polymerization of EDT in an aqueous polyelectrolyte (most commonly PSS) solution using Na$_2$S$_2$O$_8$ as the oxidizing agent. Carrying this reaction out at room temperature results in a dark blue, aqueous PEDT/PSS dispersion, which is commercially available from Bayer AG under its trade name BAYTRON P (Scheme 8). An interesting aspect of BAYTRON P is that, after drying, the remaining PEDT/PSS film is highly conducting, transparent, mechanically durable, and insoluble in any common solvent.
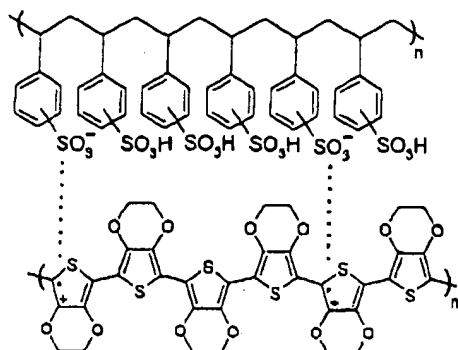
Scheme 8. PEDT/PSS blend (BAYTRON P).

BAYTRON P was initially developed for antistatic applications in the photographic industry. Nowadays, however, it serves as a multi-purpose conducting polymer blend for several applications (see Sec. 4). As a result it is available

in different grades (e.g., BAYTRON P EL (VPAI 4083) corresponds to the electronic grade of BAYTRON P that has been developed specifically for light-emitting diode (LED) applications).

While soluble alkylated PEDT derivatives (R ≥ $C_{10}H_{21}$) allow standard "solution" characterization techniques to be utilized, the insoluble PEDT and PEDT/PSS derivatives preclude molecular characterization to a great extent. Based on electronic and vibrational spectroscopy it can be determined that both compounds are conjugated species that are easily oxidized due to their electron-rich character: however, detailed structural features such as their molecular weight, polydispersity, and their end-groups remain unclear.

An important contribution to the structural characterization of PEDT was presented by Inganäs and co-workers, who were the first to propose a structural model for tosylate-doped PEDT.[52] Using de Leeuw's chemical method extended to a surface-confined polymerization,[51] they prepared thin PEDT films that were subsequently studied with grazing incidence X-ray diffraction using synchrotron radiation. From these studies they concluded that the material is very anisotropic and that there is a limited crystalline order in these thin films. Furthermore, they have evidence for a para-crystalline state with small para-crystalline regions. The same group also studied PEDT's electronic structure by X-ray and ultraviolet photoelectron spectroscopy,[53] as well as by spectroscopic ellipsometry.[51] These results suggest that PEDT prepared in this manner can be seen as an anisotropic metal.

2.3.2. Electrochemical Polymerization of EDT Derivatives

Another especially useful polymerization method utilizes electrochemical oxidation of the electron-rich EDT-based monomers. This method stands out as it requires only small amounts of monomer, short polymerization times, and can yield both electrode-supported and free-standing films.

In the case of EDT itself, electrochemical polymerization results in the formation of a highly transmissive sky-blue, doped PEDT film at the anode.[48,54] A variety of electrolytes are compatible with EDT-derivative polymerization, including polyelectrolytes, as was nicely demonstrated by Wernet and co-workers,[55] or using an aqueous micellar medium.[20,56] Similarly, substituted (alkylated, alkoxylated, alkylsulfonated, etc.) EDTs can be polymerized electrochemically, as well as combinations of different monomers.[15-17,20,21]

A slightly modified electrochemical polymerization method, electrochemical desilylation, uses α,ω-disilylated EDT-based monomers.[32a] This method, which is based on the loss of a trimethylsilyl (TMS) group, leads to polymers having the same nominal repeat unit as that obtained from polymerization of the parent monomers. Two benefits stand out in using bis-TMS-derivatized monomers. First, the films formed adhere more strongly to oxide-based elec-

trode surfaces (indium tin oxide (ITO), Au, etc.) giving them enhanced switching properties. In addition, as more complex and larger multi-ring monomers are prepared, TMS derivatization increases their solubility greatly, therefore, improving their polymerization characteristics.

### 2.3.3. Transition Metal–Mediated Coupling of Dihalo Derivatives of EDT

Many thiophene-based polymers have been prepared over the years using transition metal–catalyzed coupling of activated organometallic derivatives.[57] Yamamoto et al. recently applied this methodology to the direct formation of neutral PEDT.[58] Though this method yields materials with low molecular weight, it may prove especially interesting when it is applied to monomers with solubilizing side groups.

2.4. Copolymers Based on 3,4-Ethylenedioxythiophene

Copolymers based on EDT can be prepared using both chemical and electrochemical polymerization routes. The bis-EDT–arylene derivatives mentioned above have mostly been polymerized electrochemically.[36,59] Concerning the chemically polymerized copolymers, there are several different methods, ranging from the standard FeCl$_3$ type to the metal-mediated cross-coupling methodology.[49,60] Of special note in the preparation of hybrid-type EDT-based polymers is the work by Elsenbaumer and co-workers, who applied the precursor polymer route to poly(EDT–vinylene)s.[61] These vinylene polymers exhibit slightly reduced bandgaps relative to PEDT itself due to relief of the interring steric interactions. To date, little has been done to exploit the synthesis of true A–B copolymers based on EDT units. This promises to be an area of extensive research in the future.

3. Properties of PEDT Derivatives

Examining the range of polymers that have been accessed using the PEDT building block, one is struck by its synthetic flexibility and utility. Its highly electron-rich nature plays a profound role in the optical, electrochemical, and electrical properties of the resultant polymers. The conducting form of PEDT stands out for its high degree of visible light transmissivity and concurrent environmental stability, which is important for industrial applications. EDT polymerizes rapidly and efficiently, leading to highly electroactive PEDT films that adhere well to typical electrode materials and have a low oxidation potential, which provides for facile, long-term electrochemical switching. As illustrated by the many derivatives shown above, PEDT provides materials with a range of bandgaps, yielding films having colors over the entire spectral range. Here, we address the properties of the neutral state, followed by the

oxidatively doped and conducting forms, and finally address the redox switching properties of PEDT and its derivatives.

3.1. Neutral PEDT and Derivatives

PEDT exhibits an electronic bandgap, defined as the onset of the π–π^* absorption, of 1.6–1.7 eV and a λ_{max} of ca. 610 nm, making it deep blue in color.[10] Due to its low oxidation potential, thin films of neutral PEDT must be handled carefully as they oxidize rapidly in air. Solutions of the alkyl derivatives (9,10), prepared via oxidative polymerization, are sufficiently stable to allow molecular and macromolecular characterization,[15,16] mentioned earlier. These solutions show an absorption onset at 1.8 eV and a λ_{max} at 575 nm (2.15 eV) since the polymer is more conformationally disordered than in the film form. The soluble PEDT derivatives can be solution processed by casting and spraying methods. Due to the air instability of these neutral PEDT derivatives, handling under an inert atmosphere is required. Ultimately, the development of organic-soluble conducting forms of PEDT materials will prove especially useful.

3.2. Bandgap Control in PEDT and Derivatives

The synthetic flexibility of EDT, coupled with its recent commercial availability as BAYTRON M, has made it an excellent component for variable-bandgap conjugated polymers. In general, the electronic bandgap of a conjugated chain is controlled by varying the degree of π-overlap along the backbone via steric interactions, and by controlling the electronic character of the π-system with electron-donating or accepting substituents. The latter is accomplished by using substituents and co-repeat units that adjust the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the π-system. A broad family of EDT-based polymers has been prepared with higher energy gaps than the parent PEDT. By using a series of oxidatively polymerizable bis-EDT–arylenes (26), polymers with bandgaps ranging from 1.4–2.5 eV have been prepared. As such, neutral polymers with colors ranging from blue through purple, red, orange, green, and yellow have been made available. This is illustrated in Figure 3, which shows the rainbow of colors possible in PEDT derivatives.

To demonstrate bandgap control, a few of the examples reported include spacers of vinylene ($E_g = 1.4$ eV), 2,5-dialkoxyphenylene ($E_g = 1.75$ to 2.0 eV), biphenyl ($E_g = 2.3$ eV), dialkylfluorene ($E_g = 2.3$ eV), and carbazole ($E_g = 2.5$ eV), proving the versatility of this method.

In addition, EDT has been used as a component in complex monomers that can provide polymers with bandgaps lower than that of the PEDT parent. For example, monomer 33, having a cyano vinylene (CNV) acceptor unit as a
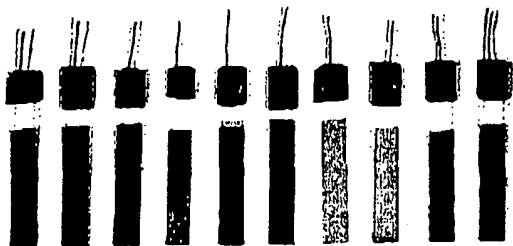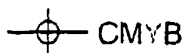
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Fig. 3. Photograph of variable bandgap EDT-based copolymers, demonstrating the range of accessible colors.

Fig. 4. Conductivity of PEDT/PSS/PVP blends at different compositions, untreated (□) and treated (●) with 0.25 M aq. MgSO$_4$ solution [64].

conjugated spacer between two EDT units, yields a polymer PBEDT–CNV (where the B in PBEDT stands for bis) with an E_g of approximately 1.1–1.2 eV. Further work using a donor–acceptor methodology has led to bis-EDT–pyridine polymers that can be both p- and n-type doped and provide for multi-color (three-state) electrochromism.[62] Especially low bandgap polymers have been prepared by combining the electron-rich EDT unit with a thienopyrazine unit, which also has the possibility of being n-type doped.[40]

3.3. Conducting Properties of PEDT and Derivatives

Using the Bayer oxidative polymerization process in solution, a surface-confined chemical polymerization method, and concurrent electropolymerization/deposition methods, PEDT is prepared in its more stable doped and conducting form. Films cast from the aqueous PEDT/PSS solution (BAYTRON P) have a high degree of mechanical integrity with conductivities ranging between 1 and 10 S/cm. These films are highly stable and can be treated for up to 1000 h at 100 °C with no change in conductivity.[9] These properties, coupled with PEDT/PSS's high level of transmissivity of visible light has led to its use as an antistatic material in photographic film applications, as detailed in Section 4.1.

One method of enhancing the properties of electroactive polymers, while simultaneously preparing useful materials, is through polymer blending. For example, poly(aniline camphor sulfonic acid) (PANI-CSA) blends with poly (methylmethacrylate) (PMMA) and nylon exhibit quite high conductivities (1–10 S/cm) at relatively low (ca. 1 %) loading levels of the conducting polymer in the host.[63] This high conductivity is attributed to the formation of a continuous network of the conducting polymer, which is phase separated from the host. These concepts have been extended to PEDT/PSS blended with polar host polymers (e.g., poly(vinylpyrrolidone) (PVP)).[64] In this instance, as illustrated in Figure 4, treatment of the blend with a bivalent metal (e.g., Mg^{2+}) leads to ionic crosslinking and enhanced electrical properties at quite low (less than 10 %) loading levels. In addition, the use of crystallization-induced phase separation between PEDT/PSS with poly-(ethylene oxide) has been shown to form blends with continuous domains of PEDT/PSS, which exhibit higher con-
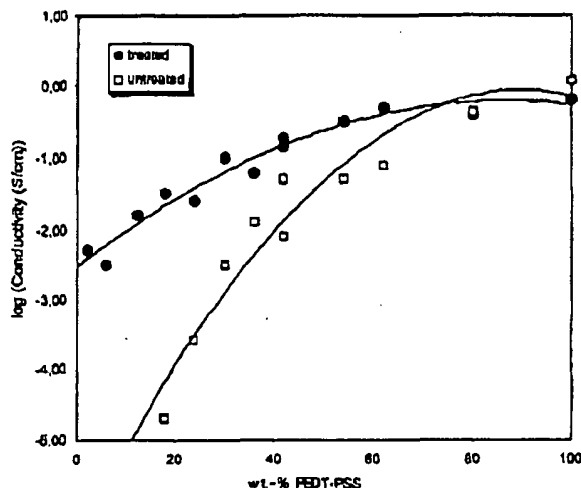
ductivities when compared to blends prepared with amorphous host polymers.[65] Conducting polymer blends may prove useful, especially in applications where concurrent control of optical and electronic properties are required. An example of this are cladding layers in electro-optic device structures. Blends of PEDT/PSS with poly(vinyl alcohol) have been used to provide a large effective poling field across a nonlinear optical (NLO) active layer, which is required for dipole orientation.[66]

Using electrochemical polymerization methods, careful control of polymerization conditions (concentration, temperature, electrode materials, etc.) allows the preparation of free-standing PEDT films using a variety of dopant anions.[67] The conductivities of these films are found to be a function of the nature of the dopant anion with room-temperature conductivities typically ranging from 10^0–10^2 S/cm. Use of PF$_6^-$ as the dopant counterion has provided especially interesting materials with high room-temperature conductivities (300 S/cm) and a temperature dependence of conductivity, which suggests the material is on the metallic side of the metal-to-insulator transition.

Use of polymeric electrolytes can also lead to PEDT films via electropolymerization and chemical polymerization.[55,68] In fact, films up to 20 m in length were prepared using a rotating stainless-steel anode. PEDT films doped with sulfated poly(β-hydroxyether) (PEDT/S–PSE) exhibit excellent mechanical properties imparted by the polyelectrolyte dopant with concurrent high conductivities in the range of 150–180 S/cm. Conductivities as high as 400 S/cm are reported when using a bis-trifluoromethyl-functionalized sulfated poly(β-hydroxyether), while the use of more flexible polymeric dopants led to films that could be elongated between 80 and 110 % when heated. In the future, promise for PEDT films with enhanced properties is held as a deeper understanding is gained of polymer/ion interactions (e.g., the use of surfactant dopant ions[67]) and
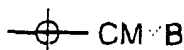
the effect of synthetic conditions on polymer structure, including molecular weight.

3.4. Electrochemistry of PEDT and Derivatives

The combination of an especially low oxidation potential and a relatively low bandgap gives PEDT some unique electrochemical and spectroscopic properties not accessible in other polymers. As the bandgap is located at the transition between the visible and near-IR regions of the spectrum, PEDT is strongly cathodically coloring and much more transmissive to visible light (sky-blue transparent) in the doped and conducting state than it is in the reduced state (deep blue).[70] The polymer exhibits a relatively broad cyclic voltammetric response with an $E_{1/2}$ of about 0.0 V vs. Ag/Ag$^+$ when being cycled between doped and undoped states, which could also be characterized by Raman spectroscopy.[71] One interesting observation is that PEDT can be electrochemically switched without the use of a conducting electrode support. Chemically deposited films were found to switch efficiently between doped and undoped states when the films were prepared on insulating polyester sheets.[72]

Examination of the spectroelectrochemical series for PEDT shows the evolution of a very strong near-IR and mid-IR[73] absorption as the polymer becomes conducting that tails strongly into the visible region. This tailing is found to be repressed in alkyl-substituted PEDT and PProDT derivatives, which greatly enhances the transmissivity of the conducting form of these polymers and increases the electrochromic contrast accessible with the films, as illustrated by Figure 5 for PProDT-Me$_2$.[15,23,48] At the same time, these derivatized PEDTs exhibit especially fast (sub-second) switching times for the large optical changes being attained.
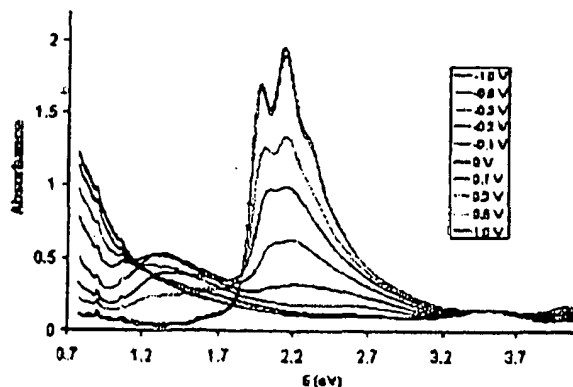

Fig. 5. Spectroelectrochemistry of PProDT-Me$_2$.

By incorporating PEDT and other EDT-based polymers into solid-state electrochemical cells, it was shown that electrochromic devices were possible with relatively small switching voltages (1.5 V), thus enabling possible applica-

tions in smart windows.[74] By using a dual polymer device construction, it was then shown that a range of colors could be accessed and devices with substantial electrochromic contrasts could also display sub-second switching times.[75] These latter devices are self-sealing to prevent ambient exposure and, as the EDT polymers have such excellent redox properties, tens of thousands of deep double switches could easily be attained.

At the present time, the PEDT family of polymers is receiving a significant amount of attention as an electrode material for a variety of applications. One of the most prevalent of these has been as a conducting buffer between the optically transparent ITO and the light-emitting or hole-transporting materials in organic and polymer LEDs.[76] PEDT has been used to improve the charge transfer rates between an electrode and a redox couple in photoelectrochemical cells.[77] Studies of PEDT electrochemistry in phosphate buffers show an especially high level of stability when compared to polypyrrole, suggesting that this family of polymers may also prove useful in biosensors and other applications using biological media.[78]

4. Present and Future Applications for Poly(3,4-ethylenedioxythiophene) Derivatives

As made obvious by the many interesting properties accessible by PEDT and its derivatives, the applications for these polymeric organic conductors will be wide-ranging.[9,12] Here we focus on those applications that have come to fruition in the commercial world. Specifically, we address its use as an antistatic coating on plastics, taking the coating of photographic film as an example, and its use as an electrode in solid electrolyte capacitors as two areas to be described in detail. Other applications will be summarized with literature references.

4.1. Antistatic Treatment of Plastics Using PEDT/PSS

Plastics tend to undergo static charging in dry air as a result of friction. Walking over synthetic carpeting can create a charge of up to several thousand volts, which is discharged when, for instance, a door handle is touched. The same effect is observed in the production and processing of photographic films during fast winding if these have not received antistatic treatment. The discharges occur with a flash of light, pre-exposing the film and making it unusable. Another field in which static charging must be avoided is the packaging of electronic components since present-day transistors and integrated circuits are irreversibly damaged by voltages in excess of 100 V.

In order to prevent these effects from occurring in practice, photographic films and packaging films for electronic components are given an antistatic treatment by increasing the conductivity of the plastic so that charge can be elimi-

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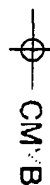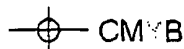
nated more readily or does not build up in the first place. In most cases, a surface resistance of $<10^9 \ \Omega/\Box$ will ensure that a plastic is antistatic.

Traditionally, films with surface resistances of $<10^{11} \ \Omega/\Box$ were obtained by coating the film substrate with ionic anti-static agents. The surface resistance of these coatings is highly dependent on the atmospheric humidity that pre-vails. In order to obtain a coating that will not be affected by atmospheric humidity, more recent developments have been directed to conducting polymers as antistatic agents, the ultimate goal being a transparent coating with a surface resistance of $<10^8 \ \Omega/\Box$. The latter should exhibit good technical properties and be environmentally friendly (e.g., avoid the use of organic solvents).

As noted earlier, chemical polymerization of EDT in the presence of aqueous PSS yields a colloidal PEDT solution that is directly suitable for aqueous processing (see Sec. 2.3.1).[11] When 20 mg of PEDT/PSS/m^2 is deposited on a polyethylene terephthalate film, a surface resistance of $10^6 \ \Omega/\Box$ is attained with an optical density of <0.01. In these coatings, the surface resistance is relatively indepen-dent of the atmospheric humidity and stability tests showed that PEDT/PSS is considerably more stable to hydrolysis, light, and temperature than other conducting polymers. These properties successfully meet the requirements for an antistatic layer for photographic film and has led to the an-nual multi-ton production of PEDT/PSS by Bayer AG. More than 100 million square meters of photographic film are coated in this way every year.

It should be noted that, apart from the antistatic treat-ment of photographic films, PEDT/PSS coatings can also be used for the antistatic treatment of other plastics,[79] as well as glass. Through the addition of appropriate binders, suitably coordinated with the particular substrate used, it is possible to achieve transparent to slightly gray coatings with a surface resistance ranging between 200 and $10^7 \ \Omega/\Box$, suggesting that this material may prove useful in many other applications.

4.2. PEDT as an Electrode Material for Solid Electrolyte Capacitors

A second application for PEDT derivatives is their use as electrodes in solid electrolyte capacitors, as illustrated schematically in Figure 6.[80]

To prepare these capacitors, the surface of an aluminum or tantalum electrode is roughened by etching or metal powder is sintered, in order to attain a high surface area electrode with a high capacitance. A thin film of metal oxide, which will serve as a dielectric, is subsequently applied to the elec-trode by anodization. A counter-electrode is finally applied to complete the capacitor. In the preparation of conventional capacitors, this last step is performed by multiple impregna-tion[81] with manganese nitrate solution and subsequent py-rolysis to form electrically conductive manganese dioxide.
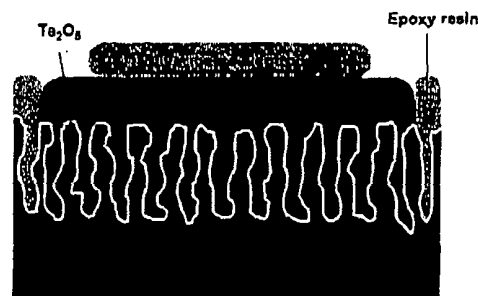

Fig. 6. Set-up of a PEDT-coated Ta/Ta$_2$O$_x$ capacitor.

As multiple steps are necessary to apply the manganese diox-ide, and its conductivity is too low to yield capacitors with good high-frequency properties, numerous attempts have been made to replace manganese dioxide by organic materi-als with higher conductivities, that are easier to apply. For this purpose Bayer AG developed a process using PEDT and a simple impregnation step as opposed to pyrolysis or elec-trochemistry.[82] In this new process, a solution of EDT and an oxidizing agent are coated onto a tantalum oxide–coated tantalum foil. Once the solvent has been evaporated the EDT polymerizes, directly forming a counter-electrode of conductive PEDT. The capacitance of such capacitors is comparable to that of similar liquid electrolyte capacitors, but the high-frequency properties are considerably better.[83]

4.3. Other Applications for PEDT Derivatives

Besides the above-mentioned applications, PEDT-based polymers are currently, and will in the future be, applied in many other applications. Examples are through-hole plat-ing of printed circuit boards,[84] antistatic coatings for cath-ode ray tubes to prevent dust attraction,[85] primers for electrostatic spray coating of plastics,[86] hole-injecting layers on ITO substrates for organic electroluminescent de-vices,[76,87] transparent electrodes for inorganic electrolumi-nescent devices (ITO replacement),[88] sensors,[38,89] re-chargeable batteries, cathode radiation tubes (CRTs),[90] photodiodes,[91] electrochromic windows,[74,75,92] corrosion protection,[93] membranes for the preparation of 4π beta radioactive sources,[94] and photovoltaic devices.[95] Of ut-most importance, these examples show that PEDT is one of the few organic conducting polymers that has success-fully found its way from a laboratory curiosity into multiple technical applications.

5. Conclusion

The research and development efforts of the past ten years have quickly brought PEDT to the forefront of the field of conducting polymers. Its properties, being its high conductivity in combination with excellent stability, a rela-tively high transparency to visible light, and aqueous pro-

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cessability of the PSS-doped form, have allowed the material to now become industrially useful. As a result PEDT and PEDT/PSS have found their way into several current applications, including as an antistatic material in photographic film, an electrode material in capacitors, and as a conducting layer in through-hole plating. The synthetic chemistry of EDT and its derivatives provides a high level of structural flexibility, which allows the properties of the resultant polymers to be varied greatly. We foresee many other applications being developed in the future specifically because these homo- and co-polymeric analogues will have carefully designed structure–property relationships. One important factor to consider in the acceptance of PEDT as a commercially useful material is its cost. Due to the lower price of pyrrole and aniline relative to EDT, polypyrrole and polyaniline can be produced in bulk, or as coatings, at a lower price to the consumer. Efforts are underway to reduce the cost of EDT through new chemistries and scale-up reductions using the present process. As this happens, even more applications will emerge, enabling PEDT and its analogues to maintain their position as the world's most applied conducting polymer.

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